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Effect of Ga-doping and UV radiation on high performance CO sensing of ZnO nano-powders

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Abstract

Pure ZnO and 3 wt.% Ga-doped ZnO nanopowders were synthesized by a simple sol–gel technique, dried in supercritical conditions and annealed at 400 °C. The effect of Ga-doping on the morphological and structural properties were evaluated by TEM and XRD. CO sensing properties of the synthesized samples were investigated, demonstrating that Ga-doping has a strong impact on CO response. The effect of UV light on electrical and sensing properties of GZO-based sensor response was also evaluated.

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Keywords: Ga-doped ZnO; Nanoparticles; Sol-gel; Gas sensor; UV Radiation; CO.

1. Introduction

Metal oxide (MOX) gas sensors have been intensively studied in the past decades for application in the detection of hazardous pollutant gases [1,2]. More recently, photoactive metal oxides have been studied by different research groups for developing high performance gas sensors. The photoactivated response of SnO_2 [3], In_2O_3 4], ZnO [5] and TiO_2 6], has been investigated under different gas atmospheres, such as CO [7] and NO_2 [3]. Due to the well-known surface conductivity of ZnO, a great deal of attention has been given to this material for gas sensors

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applications. Zinc oxide is sensitive to many gases such as CO, hydrogen, water vapor and hydrocarbons [8]. It is a photoactive materials and, furthermore, its properties can be easily modulated by doping.

Therefore, in this study, ZnO nanoparticles doped with Ga were synthesized, characterized and tested in the monitoring of low concentration of CO in air in both under dark and UV-light conditions. The monitoring of CO is of outmost importance in the environmental control, because it is a gas produced during incomplete combustion and is toxic at very low concentrations [9]. Our final aim is then to develop CO gas sensors operating at low temperature with good sensitivity to low CO concentration, in the range 5-50 ppm, and fast response/recovery time.

2. Experimental details

2.1. Samples preparation

The samples were prepared using a sol-gel route with 16 g of zinc acetate dihydrate [$Zn(CH_3COO)_2 \times 2H_2O$] as a precursor in 112 ml of methanol. After 10 min of magnetic stirring at room temperature, an adequate quantity of gallium nitrate hydrate [$GaN_3O_9 \times H_2O$] corresponding to [Ga]/[Zn] ratios of 0 and 0.03. After 15 min of magnetic stirring, the solution was placed in an autoclave and dried in supercritical ethyl alcohol (Tc = 243 °C; Pc = 63.6 bars), according to protocol reported in ref. [10]. Furthermore, the samples were annealed at a temperature of 400 °C in air for 2 hours. The samples are named G0ZO, G3ZO according the nominal Ga loading in each sample.

2.2. Characterization

The microstructure of the samples were identified by XRD (Bruker AXS D8 Advance) using the CuKα1 wavelength of 1.5405 Å. Transmission electron microscopy (TEM) performed with a JEOL JEM 2010 electron microscope (LaB_6 electron gun) operating at 200 kV and equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging was used to study the morphology of the nanopowders synthesized. The samples were prepared by placing a drop of the samples dispersed in isopropanol on 400 mesh holey-carbon coated copper grids.

3. Results and discussion

3.1. Morphological and microstructural characterization

XRD spectra of pure and doped samples reported in Fig.1a,b show the diffraction peaks of hexagonal wurtzite ZnO. The addition of Ga causes a shift of all diffraction peaks at the highest 2θ value, that is in agreement with the smaller ionic radius of Ga^{+3} (0.62 Å) compared to Zn^{2+} one (0.74 Å). Further, Ga doping appears to decrease the intensity of diffraction peaks.

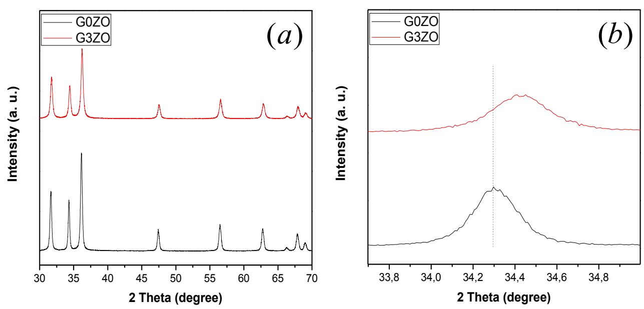

Fig. 1. a) X-ray diffraction spectra of synthesized samples after annealing at 400°C for 2 h. Main peaks are indexed according to JCPDS card 36-1451 (hexagonal wurtzite structure). b) Enlargement of the peak at 34.25 2-theta.

Fig. 2a reports a typical TEM image taken from the undoped ZnO annealed at 400°C. Small ZnO NPs having size in the nanometer range are observed. The crystallites present a prismatic-like shape with a narrow particle size distribution. TEM analysis shows the same morphology and particle size on the Ga-doped samples (Fig. 2b).

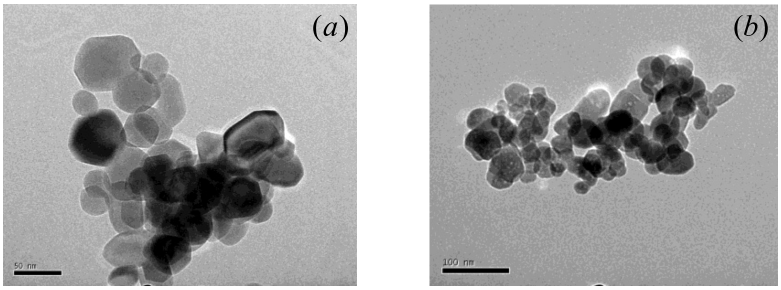

Fig. 2. TEM pictures of: (a) G0ZO ; (b) G3ZO.

3.2. Sensing tests

The sensing properties of the GZO samples towards CO detection at low concentrations (5-50 ppm) in air were initially investigated temperatures in dark conditions. Fig. 3 summarizes the data obtained and reports the responses of the sensors to 50 ppm of CO versus the operating temperature from 150°C to 400 °C. At the lowest temperature tested, 150 °C, the response is almost negligible on both samples. The response however increases with the temperature. The ZnO sample doped with Ga shows the better sensing properties, with a maximum of sensitivity at around 250 °C.

The samples were then compared under UV light illumination. It has preliminary found that UV illumination decreases the baseline resistance, likely due to the generation of free charge carriers. This effect is especially noted at low temperature, because, in addition to the optical excitation, thermal activation also leads to an increase of free charge carriers in the conduction band of ZnO which superimposes the effect of the optical activation at higher temperature. Fig. 4 shows the GZO sensors in dark and under UV light at 200°C. It can be noticed as pure ZnO is little affected by UV illumination, whereas the effect of UV on the sensitivity is remarkable on the doped sample.

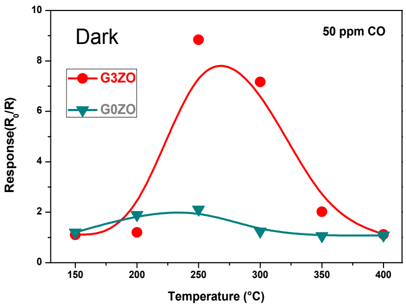

Fig. 3. Response to 50 ppm CO of the GZO sensors as a function of the temperature in dark

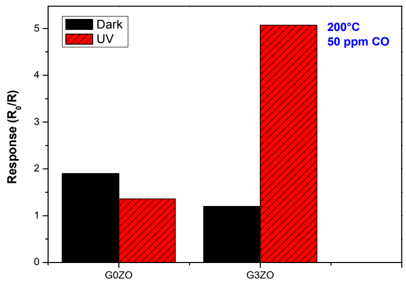

Fig. 4. Comparison of the response of the GZO sensors in dark and under UV light.

MOX gas sensors usually works at high temperature, ranging from 200°C to 400°C, but this require many energy demanding [11]. It is known that UV light may facilitates gas-sensing measurements at lower temperatures [12].

Then, we tried to increase the response of our sensors to lower temperatures. Fig. 5 shows the transient response of Ga-doped sensor. Good response with fast response/recovery times was obtained at 150 °C demonstrating the positive effect of combining Ga-doping and UV light in enhancing the sensing characteristics of ZnO nanoparticles.

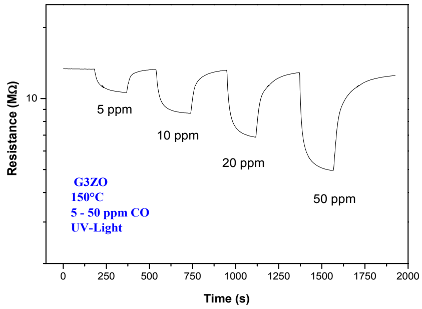

Fig. 5. Dynamic response to CO of G3ZO sensor operating at 150 °C with UV light.

4. Conclusion

A study on the effect of Ga-doping and UV radiation on the CO sensing properties of ZnO gas sensor has been carried out. We demonstrated that UV radiation enhances significantly the sensitivity of Ga-ZnO gas sensor. Also, the resistance of the metal oxide thick films decreases due to the UV radiation compared to the case when there is no UV radiation. Further study will be aimed at optimize the composition of this interesting sensing system.

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